Exponential decay of relaxation effects at LaAlO$_3$/SrTiO$_3$ heterointerfaces

U. Schwingenschlögl and C. Schuster

Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany

Abstract

We study the decay of interface induced structural and electronic relaxation effects in epitaxial LaAlO$_3$/SrTiO$_3$ heterostructures. The results are based on first-principles band structure calculations for a multilayer configuration with an ultrathin LaAlO$_3$ layer sandwiched between bulk-like SrTiO$_3$ layers. We carry out the structure optimization for the heterointerface and investigate the electronic states of the conducting interface layer, which is found to extend over two SrTiO$_3$ unit cells. The decay of atomic displacements is analyzed as a function of the distance to the interface, and the resulting exponential law is evaluated quantitatively.

Heterostructures based on perovskite transition metal oxides have attracted great attention in the last decades [1, 2], particularly due to the discovery of extraordinary electronic and magnetic properties of the internal interfaces. For example, a quasi two-dimensional electron gas (2DEG) with an unexpected high charge carrier density develops at the contact between the two band insulators $LaAlO_3$ and $SrTiO_3$ [3, 4], despite of sizeable band gaps of $5.6\,eV$ and $3.2\,eV$ [5, 6]. The $LaAlO_3/SrTiO_3$ heterointerface therefore has been subject to intensive research in recent years [7, 8, 9]. From the structure point of view it comprises $(SrO)^0$, $(TiO_2)^0$, $(LaO)^+$, and $(AlO_2)^-$ layers, where the electron-doped $(TiO_2)^0/(LaO)^+$ contact gives rise to the 2DEG. Moreover, the contact between a Mott insulator and a band insulator can likewise show conductivity, as realized in the $LaTiO_3/SrTiO_3$ heterostructure [10]. In all these cases, the phenomenon of conductivity has to be attributed to electronic relaxation, because the local charge distribution and its alterations close to the interface are the main ingredients. Local deviation from the bulk crystal structure as well as a transfer of charge across the interface, induced by different electrochemical potentials in the component materials, hence will play a key role for the formation of conduction states [11].

Electronic relaxation usually is accompanied by a fundamental lattice relaxation. The influence of structure modifications on the $LaTiO_3/SrTiO_3$ interface has been stressed by Hamann *et al.* [12], comparing experimental data to results from electronic structure calculations. In addition to the initial formation of the conduction layer, the mobility of the charge carriers likewise depends critically on structural details, such as the incorporation of O-vacancies. For the $LaAlO_3/SrTiO_3$ interface, the mobility increases strongly with the vacancy concentration [13]. Nevertheless, conductivity is maintained in the stoichiometric case. Pulsed laser deposition techniques and molecular beam epitaxy nowadays, in principle, make it possible to grow layered structures with a precision of a single unit cell, and therefore to create atomically sharp interfaces. Local structural and electronic properties of such contacts between two perovskite oxide compounds, in general, differ strikingly from the bulk materials, similar to the reconstruction and formation of specific electronic states at surfaces [14].

Interface atomic structures often are resolved by x-ray diffraction techniques. A contact of $LaAlO_3$ and $SrTiO_3$ layers, for instance, is characterized by displacements of the anions and cations in opposite direction, because of Jahn-Teller distorted TiO_6 octahedra [15]. Data of the Ti^{3+}/Ti^{4+} mixture in the vicinity of the contact suggest, that we actually have
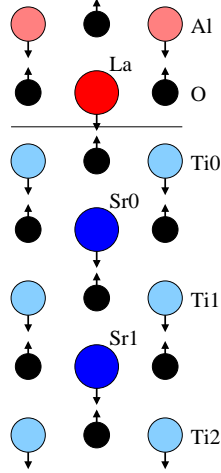
FIG. 1: (Color online) Schematic view of the $LaAlO_3/SrTiO_3$ heterostructure, in a projection along the [100] direction and perpendicular to the interface plane. Arrows show the directions of atomic shifts due to the interface lattice relaxation.

no atomically sharp interface, but a metallic $La_{1-x}Sr_xTiO_3$ layer is formed [16]. Moreover, conducting tip atomic force microscopy ensures that the metallicity is confined to a rather thin region of $\approx 50\,nm$ extension [17]. From the theoretical point of view, first principles electronic structure calculations using density functional theory (DFT) are a powerful tool for studying a structural reconstruction. Results have been reported in the literature for the $LaAlO_3/SrTiO_3$ [18, 19, 20] and the $LaTiO_3/SrTiO_3$ interface [12, 21]. An elongation of the TiO_6 octahedra is found to be a common feature, in accordance with experimental data. Electron doping of Ti ions, in combination with the Jahn-Teller effect, leads to the appearance of metallicity in a band structure calculation applying the local density approximation (LDA). Considering the local electron-electron interaction more accurately by means of the LDA+U scheme, Pentcheva and Pickett [22] have succeeded in obtaining a ferromagnetic spin order, tracing back to occupied d_{xy} orbitals in a checkerboard of Ti^{3+} sites.

While structural distortions have been investigated in detail for different interfaces, an analysis of their decay perpendicular to the contact plane is missing so far, although a rather general behaviour is to be expected for a large class of materials. The work of Hamann *et al.* [12] includes data about the atomic displacements but not a systematic characterization. Furthermore, the variation of the electrostatic potential across the $LaAlO_3/SrTiO_3$ interface is discussed in [18]. Beyond these data, investigation of structural details as a function of the distance to the interface and, in particular, their interrelations to the electronic states is of

special interest for a quantitative description of transport processes. In order to solve these questions, our present study deals with multilayer structures consisting of a thin $LaAlO_3$ domain contacted to a bulk-like $SrTiO_3$ domain, which allows us to quantify the decay of the structural and electronic relaxation effects within the titanate. We carry out a structure optimization for the full heterointerface to give a spacially resolved characterization of the electronic states. In particular, our data point at an exponential law for the suppression of the interface-induced distortion, for which we evaluate the (structural) screening length in detail. Comparison to an electrostatic model then enables us to obtain insights into the strength of the electronic screening in perovskite-based transition metal oxides.

Our findings rely on the generalized gradient approximation (GGA), where we use the Wien2k code [23] with a mixed linear augmented-plane-wave (APW) and APW plus local-orbitals basis set. The package is particularly suitable for describing interfaces [24, 25]. In all calculations the charge density is represented by $\approx$27,000 plane waves. In addition, the **k**-space grid has 21 points in the irreducible wedge of the Brillouin zone and the Perdew-Burke-Ernzernhof parametrization is used. The basis set for the expansion of the wave functions contains the valence states La $6s$, $6p$, $5d$, Sr $5s$, $5p$, Ti $4s$, $4p$, $3d$, Al $3s$, $3p$, and O $3s$, $3p$, and the semi core states La $5s$, $5p$, Sr $4s$, $4p$, Ti $4s$, $4p$, Al $2p$, and O $2s$. We set up a tetragonal supercell by stacking 20 perovskite unit cells: A layer of two $LaAlO_3$ unit cells in the center of the supercell is sandwiched between bulk-like $SrTiO_3$ layers, which both consist of nine unit cells. In total, the supercell contains 42 inequivalent atomic sites. In the ab-plane, i.e. the interface plane, and in the c-direction the lattice constant is set to 3.905 Å, i.e. the value of bulk $SrTiO_3$. We deal with an n-type interface with $(TiO_2)^0/LaO^+$ stacking.

The atomic structure of the $LaAlO_3/SrTiO_3$ supercell is illustrated schematically in Fig. 1 in a projection along the [100] axis, where the interface plane is oriented perpendicular to the stack. For convenience, we have numbered the Ti and Sr sites according to their distance to the interface. In Fig. 2 we show the partial Ti $3d$ DOS calculated for the Ti0 and Ti3 atoms of our heterointerface, respectively. These data are compared to the bulk Ti $3d$ DOS. Because of a charge transfer off the $LaAlO_3$ layer and, consequently, electron doping of the Ti atoms in the vicinity of the interface, the Ti0 $3d$ DOS shifts to lower energy, with respect to the bulk DOS, and conduction states are formed. As these states are characterized by a remarkable (quasi) two-dimensional dispersion, they are attributed
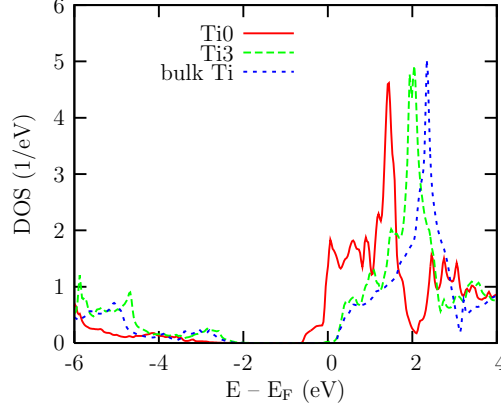
4

FIG. 2: (Color online) Partial Ti $3d$ DOS (per atom) for the interface atoms (Ti0) and the atoms in the 4th TiO_2 plane off the interface (Ti3), see Fig. 1. The corresponding Ti $3d$ DOS of bulk $SrTiO_3$ is shown for comparison.
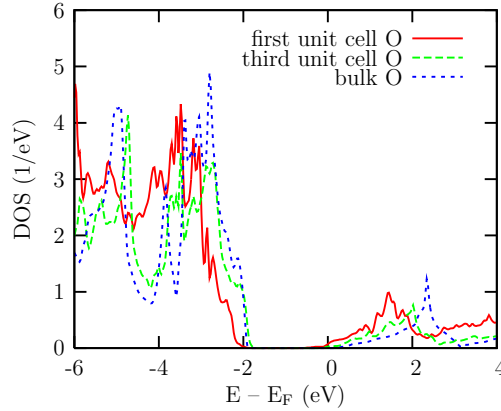

FIG. 3: (Color online) Comparison of partial O $2p$ DOS data (per atom) for the O atoms in the first and third $SrTiO_3$ unit cell off the interface and bulk $SrTiO_3$.

to a 2DEG [9], in accordance with experimental findings. However, for a growing distance to the interface the doping amplitude declines rapidly, which is visible in Fig. 2 for the Ti3 site: conduction states have disappeared. We mention that for the neighbouring Ti2 site a small but finite DOS remains at the Fermi energy. Moreover, since even the gross shape of the Ti3 DOS is similar to the bulk DOS, interface effects have vanished.

Conduction states therefore are restricted to a narrow area of only two $SrTiO_3$ unit cells, i.e. three TiO_2 planes. However, due to electronic correlations beyond the GGA which tend to increase band gaps, this restriction even is only an upper boundary for the extension of the electron gas. Our line of reasoning is supported by the O $2p$ DOS depicted in Fig. 3. The
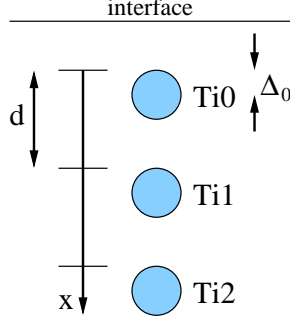
FIG. 4: (Color online) Setup of the electrostatic model.

data again refer to the first and third SrTiO$_3$ unit cell off the interface and are compared to the bulk DOS. While close to the LaAlO$_3$ contact the O electronic structure reveals serious deviations from the bulk state, only minor differences are left for the O sites in the third unit cell.

The dependence of the structure relaxation on the distance of an atom from the interface can be described by a merely electrostatic model. Assuming that all the atomic shifts are directed perpendicular to the contact plane, we decompose the system into Ti, Sr, and O chains running in this direction. The equilibrium position $\Delta = 0$ of any atom then is determined by the minimum of the electrostatic potential $u(\Delta)$ due to its nearest neighbours,

$$4\pi\epsilon_0 u(\Delta) = (d + \Delta)^{-1} + (d - \Delta)^{-1},$$

where d denotes the nearest neighbour distance. In harmonic approximation, the atomic force as function of the displacement from equilibrium therefore is

$$F(\Delta) = -\frac{4}{4\pi\epsilon_0 d^3}\,\Delta.$$

Let x denote the distance of an atom from the first atom of its chain at the interface, see Fig. 4, which is subject to the initial displacement $\Delta(x = 0) = \Delta_0$. We obtain

$$-\frac{4}{d^3}\,\Delta(x) = F_+(x) - F_-(x),$$

where $F_\pm(x) = d^{-2} - (d - \Delta(x \mp d))^{-2}$ represents the forces of the two neighbours acting on an atom near the interface. A Taylor expansion up to first order gives

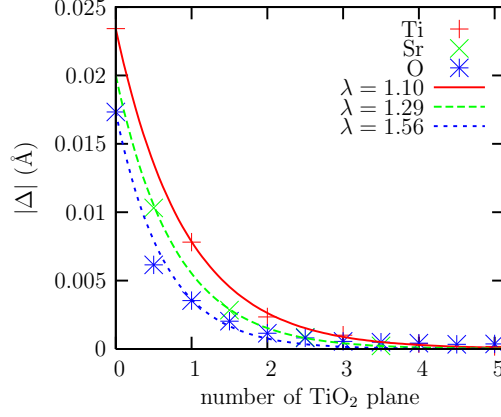$$-4\Delta(x) = 2\Delta(x + d) - 2\Delta(x - d) = 4d\Delta'(x),$$

6

FIG. 5: (Color online) Calculated displacements in the fully relaxed heterostructure given as a function of the distance to the interface TiO_2 plane. The numbering of the TiO_2 planes is illustrated in Fig. 1.
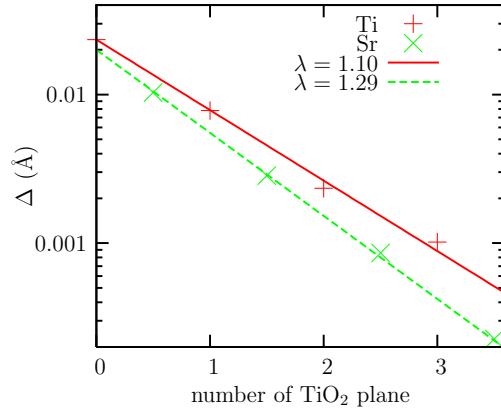

FIG. 6: (Color online) Logarithmic plot of the data from Fig. 5. A nearly ideal exponential dependence on the distance to the interface is obtained for the magnitudes of the Ti and Sr atomic displacements.

and hence $\Delta(x) = \Delta_0 \exp(-d^{-1}x)$. Electronic screening is expected to modify the exponential decay according to

$$\Delta(x) = \Delta_0 \exp(-\lambda \cdot x),$$

where we set $d = 1$ and introduce an effective structural screening length $\lambda > 1$.

The Ti and O atomic displacements found in our heterostructure after the structure optimization are shown in Fig. 5 as functions of the distance to the interface, in each case given via the number of the TiO_2 plane a site belongs to. Moreover, Fig. 5 includes the displacements of the interstitial Sr atoms. The amplitudes of all these shifts are largely

consistent with our model. Specifically, we observe a nearly perfect exponential decay of the displacements with structural screening lengths of $\lambda = 1.10$ for the Ti, $\lambda = 1.29$ for the Sr, and $\lambda = 1.56$ for the O sites. Corresponding fit curves are shown in Figs. 5 and 6, where the logarithmic representation of the curves in Fig. 6 stresses that deviations from the exponential law are negligible for both Ti and Sr. They are slightly larger for the O sites. The full deformation pattern induced by the interface lattice relaxation is shown in Fig. 1. As the Ti and O atoms are shifted in opposite direction, the experimental Jahn-Teller distortion of the TiO_6 octahedra at the interface is reproduced by our data [15].

The maximal amplitude of the displacements amounts to $\Delta_0 = 0.023\,\text{Å}$ for the Ti and $\Delta_0 = 0.017\,\text{Å}$ for the O atoms, as realized for the interface TiO_2 layer. Furthermore, extrapolation of the Sr data to this layer leads to a value of $\Delta_0 = 0.020\,\text{Å}$, which seems to reflect a similar interface effect on the different atomic species. However, whereas the Ti and Sr sites move off the interface plane, the O sites approach it. For this reason, we have a relative shift between the Ti/Sr and the O sublattice, which is (exponentially) suppressed in the $SrTiO_3$ bulk. Consequently, the structural prerequisites for the formation of a 2DEG are fulfilled only in the vicinity of the interface plane. In the third TiO_2 layer off the contact relaxation effects have decayed to less than 4% of their initial amplitude, which explains our previous observation that no conduction states are formed here as well as in any layer farther away from the contact. Deviations of the structural screening length from the value $\lambda = 1$, as expected in the electrostatic picture, amount to 10% and 29% for the Ti and Sr sites, respectively. They can be attributed to the electronic screening, whereas the quicker decay of the O displacements is connected to the potential of the O octahedra to evade mechanical stress via distortions.

In conclusion, we have presented first-principles band structure results for a prototypical $LaAlO_3/SrTiO_3$ heterointerface. In general, the electronic properties of heterostructures are closely related to the structural distortions affecting the component materials. By means of a detailed structure optimization we have investigated the length scala on which such distortions are suppressed in the bulk materials. We find that the decay of structural relaxation effects is well described by an exponential law, in agreement with electrostatic considerations. However, the structural screening length λ is significantly reduced due to electronic screening. We expect that these results are fairly independent of the compounds forming the interface, as specialties of the chemical bonding are found to play a less important role for

the structural screening. In the LaAlO$_3$/SrTiO$_3$ heterostructure the formation of a metallic layer is restricted to a narrow area next to the interface, comprising only two perovskite unit cells.

---

[1] H. Kroemer, Rev. Mod. Phys. **73**, 783 (2001).

[2] C.H. Ahn, J.-M. Triscone, and J. Mannhart, Nature **424**, 1015 (2003)

[3] A. Ohtomo and H.Y. Hwang, Nature **427**, 423 (2004).

[4] A. Ohtomo and H.Y. Hwang, Nature **441**, 120 (2006).

[5] P.W. Peacock and J. Robertson, J. Appl. Phys. **92**, 4712 (2002).

[6] K. van Benthem, C. Elsässer, and R.H. French, J. Appl. Phys. **90**, 6156 (2001).

[7] S. Thiel, G. Hammerl, A. Schmehl, C.W. Schneider, and J. Mannhart, Science **313**, 1942 (2006)

[8] W. Siemons, G. Koster, H. Yamamoto, T.H. Geballe, D.H.A. Blank, M.R. Beasley, Phys. Rev. B **76**, 155111 (2007).

[9] U. Schwingenschlögl and C. Schuster, Europhys. Lett. **81**, 17007 (2008).

[10] A. Ohtomo, D.A. Muller, J.L. Grazul, and H.Y. Hwang, Nature (London) **419**, 378 (2002).

[11] S. Okamoto and A.J. Millis, Nature **428**, 630 (2004).

[12] D.R. Hamann, D.A. Muller, and H.Y. Hwang, Phys. Rev. B **73**, 195403 (2006).

[13] G. Herranz, M. Basletić, M. Bibes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, J.-L. Maurice, A. Hamzić, J.-P. Contour, A. Barthélémy, A. Fert, Phys. Rev. Lett. **98**, 216803 (2007).

[14] U. Schwingenschlögl and C. Schuster, Chem. Phys. Lett. **449**, 126 (2007); Eur. Phys. J. B **60**, 409 (2007); Europhys. Lett. **81**, 26001 (2008).

[15] V. Vonk, M. Huijben, K.J.I. Driessen, P. Tinnemans, A. Brinkman, S. Harkema, and H. Graafsma, Phys. Rev. B **75**, 235417 (2007).

[16] P.R. Willmott, S.A. Pauli, R. Herger, C.M. Schlepütz, D. Martoccia, B.D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca, and Y. Yacoby, Phys. Rev. Lett. **99**, 155502 (2007).

[17] M. Basletic, J.-L. Maurice, C. Carretero, G. Herranz, O. Copie, M. Bibes, E. Jacquet, K. Bouzehouane, S. Fusil and A. Barthélémy, arXiv:0710.1395 (2007).

[18] J.-M. Albina, M. Mrovec, B. Meyer, and C. Elsässer, Phys. Rev. B **76**, 165103 (2007).

[19] M.S. Park, S.H. Rhim, and A.J. Freeman, Phys. Rev. B **74**, 205416 (2006).

[20] S. Gemming and G. Seifert, Acta Mat. **54**, 4299 (2006).

[21] S. Okamoto, A.J. Millis, and N.A. Spaldin, Phys. Rev. Lett. **97**, 056802 (2006).

[22] R. Pentcheva and W.E. Pickett, Phys. Rev. B **74**, 035112 (2006).

[23] P. Blaha, K. Schwarz, G. Madsen, D. Kvasicka, and J. Luitz, *WIEN2k: An augmented plane wave and local orbitals program for calculating crystal properties* (Vienna University of Technology, Austria, 2001).

[24] U. Schwingenschlögl and C. Schuster, Europhys. Lett. **77**, 37007 (2007); Appl. Phys. Lett. **90**, 192502 (2007).

[25] C. Schuster and U. Schwingenschlögl, J. Appl. Phys. **102**, 113720 (2007).